

# Plastic wastes to Energy. Pyrolysis Simulation by Thermogravimetry

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## ABSTRACT

The world is finally waking up to the plastic problem which is like a ticking time bomb set to explode with the increasing amount of plastic waste that is been generated daily. This research work studied the thermal degradation of plastic waste and kinetic modelling process which can be useful in the determination of key operating design and parameters.

Kinetic modelling requires significant amount of information about kinetic parameters, especially the activation energy. Thermogravimetric analysis (TGA) was used to obtain kinetic data with degradation taking place in a single step process. The kinetic analysis was studied by conventional thermogravimetric technique (Direct Arrhenius Method, Coat & Redfern and Horowitz and Metzger) with single heating rate(30°C/min) in nitrogen atmosphere for the different plastic waste. The activation energy obtained using the different approach for the plastic ABS\_White, ABS\_Blue, ABS (30) PS, LDPE, NYLON and PET was (219, 240, 188, 222, 260, 175, 304), (226, 189, 224, 382,275,186, 347) KJ/mol respectively. The result obtained using these models were in accordance with published data, however these models use unrealistic assumptions that may not be accurate in predicting the true degradation behavior of the polymer, hence it cannot give a proper understanding of how pyrolysis occur and how the process can be optimized thus the reason for the distributed activation energy analysis model (DAEM)

The DAEM algorithm was developed using MATLAB with data obtained from TGA experiments which was used in calculation of kinetic parameters. The results obtained from the simulation were able to effectively model the degradation behavior of the different plastics in this study, thus, predicted the thermal behavior of plastics at different heating rates.

**Keywords:** Plastic wastes; Pyrolysis Kinetics; Thermogravimetry; Distributed Activation Energy Model.

## 1. INTRODUCTION

Society throw-away culture, which is strongly influenced by consumerism, is steadily increasing the amount of waste generated. The amount and type of waste generated is determined by rate of urbanization, level of economic development and population growth. According to (WorldBank, 2019), the world generates 2.01 billion tonnes of Municipal Solid Waste which corresponds to the waste generate per person per day ranging from 0.11 – 4.54kilograms. Annual waste generated is expected to increase by 70% to about 3.4 billion tonnes in 2050 due to rapid increase in population and urbanization.

Plastics contribute to approximately 10% of discarded waste (Geyer, 2017) and only about 25% is being recycled Plastic wastes are non-homogeneous group of materials that differ not only with regards to their chemical composition or previous application field, but also quality, (purity or contamination level). All those issues influence the future treatment possibilities. Plastics key strengths are its durability and versatility. However, these strengths have become its greatest

weakness which is its non-degradability. This is the plastic paradox.

### Plastic Waste Impact

Looking at the world today, 1 million plastic drinking water bottles are purchased every minute while about 5 trillion single use plastic bags are used worldwide annually. This simply means half of all plastics produced is designed to be used just once and thrown away. (Day, 2018) This is causing an adverse effect on our ecosystem.

### Impact on Environment

**Oceans:** The distribution and accumulation of ocean plastics is strongly influenced by oceanic surface currents and wind patterns. Plastics are typically buoyant; thus, they can be easily transported by the prevalent wind and surface current routes. These plastics tends to accumulate in oceanic gyres, with high concentrations of plastics at the center of ocean basins and much less around the perimeters.

**Land:** Plastics containing chlorine as additives, could release harmful chemicals into the soil which may later seep into groundwater, contaminating it. This could cause serious harm to living organism that drinks the water. Landfill as a form of waste management,

contains different types of plastics. Microorganism, that facilitates the biodegradation of plastics, breaks this complex polymer, thereby releasing methane which is a greenhouse gas that severely contributes to global warming.

### **Impacts on Animals**

On a yearly basis, ocean plastic is estimated to kill millions of marine animals. About 700 species including endangered ones are affected by this problem. Marine species of all sizes, from zooplankton to whales, now eat microplastics. Plastic wastes impact on wildlife is by three main pathways (Law, 2017). These are by entanglement, ingestion and interaction.

### **Impacts on Humans**

Additives that are added in plastic production, may have harmful effect that could be carcinogenic or promote endocrine disruption. Additive such as phthalate plasticizers and brominated flame retardants via biomonitoring, have been identified in human population (Barnes, Galgani, Thompson, & Barlaz, 2009). Some chemicals in plastics has been deemed the leading cause of disruptions in fertility, reproduction, sexual maturation, and other health effects. (North & Halden, 2013)

### **Plastic Waste Management**

The incitation of plastic waste management; recycling and incineration started around 1980, before then, after use, plastic waste was probably sent to landfill or discarded indiscriminately. During incineration of plastics, this process could lead to loss of oxygen and incomplete combustion may occur which may generate poisonous gases like dioxins and this can adversely affect human health. Due to the growing environmental concerns, landfill as a disposal process is being frowned upon and other methods such as gasification, pyrolysis and biodegradation seems like the best option.

### **Plastic Waste to Energy**

Energy plays an important role in the life cycle of plastics. With the increasing demand for energy, the world is faced with finding the right fuel that would not deplete finite stock but also reduce environmental concerns. At the end of the life of plastics, the energy used in the production should be recovered by appropriate waste management technique such that plastic waste is seen as a valuable material from the resources conservation's point of view and a good waste management can contribute to sustainable development. Pyrolysis seems to be the most suitable method in terms of economics in solving the steadily increasing growing amount of plastic waste and meeting the growing energy demand. This is made

possible by producing liquid fuel with similar properties to commonly use fossil fuel thereby limiting the world dependence finite hydrocarbon resources.

Pyrolysis is the thermochemical decomposition of large molecular weight polymer carbon in the absence of oxygen to produce smaller molecular weight fractions. This decomposition process may occur by removal of small molecules, depolymerization or random cleavage (Silvério, 2008). This process is usually endothermic thus, it requires the supply of heat for the reaction to occur (Buekens, 2006). Pyrolysis can be carried out at different temperatures, heating rate, reaction times, pressures, in the presence or absence of catalysts and reactive gases. The various operating conditions have a great influence on the type of product obtained and the volume of the yield. The product obtained includes gas, liquid consisting of paraffins, olefins, naphthenes and aromatics and solid (char).

### **Chemical Composition of Plastics**

Plastics are used for different purposes thus its composition may differ. These compositions are reported in terms of proximate analysis. Proximate analysis is a technique that is used to measure the chemical properties of the plastic compound based on moisture content, fixed carbon, volatile matter and ash content (Kreith, 1998). Volatile matter and ash content are the major factors that influence the liquid and gas yield in pyrolysis process. High volatile matter indicates the high liquid oil production and a high ash content decreases the liquid production but increases the gaseous yield and char formation (Abnisa F, 2014).

### **Degradation Reaction Mechanism**

Plastics thermal degradation is the breaking down of long polymer chains into smaller fractions and this process can be quite complex because it could be influenced by different factors. When plastics is subjected to high temperatures, its physical properties changes. Plastics undergoes three major thermal transitions with increasing temperature these are; glass transition, the melting, and decomposition. At room temperature, all polymers are hard solids, (glassy state.) As the temperature increases above glass transition temperature,  $T_g$ , the plastic gets enough energy to that allows the chains to move freely and becomes rubberlike (Wunderlich, 2005). As temperature further increases, the rubberlike plastic is changed to liquid-like substance when this temperature rises above the melting temperature,  $T_m$ , the plastic starts to decompose. When the decomposition temperature  $T_p$  is reached, the phenomena can be described by changes in elastic modulus of the plastics. When the temperature rises

above the plastics decomposition temperature, the plastics undergoes a chemical change which facilitate the cracking process. As the temperature keep increasing, vibration of the molecules keeps increasing until it gets to a point whereby it can overcome the Van der Waals force this process is called evaporation. However, if the induced energy due to the Van der Waals force is greater than the bond enthalpy between the molecules, cracking of the molecules would occur instead of evaporation. Cracking in the molecular structure generally occurs at the most unstable bonds. For plastics, differences in the carbon bond molecular structure influences the stability of the carbon bond as shown in (Wade, 1995). Bond dissociation energy is the energy required to break bonds. This is the energy when the Van der Waals force induced energy is equal to the bond enthalpy. The bond dissociation energies for C-C bond of primary, secondary, and tertiary carbons are 355, 351, and 339kJ/mol, respectively (McMurry, 2000) . There are three types of cracking mechanism that occurs during plastic pyrolysis (Lee, 2006). These are random cracking, chain strip cracking and end chain cracking

### Pyrolysis Reaction Stages

During plastic pyrolysis, numerous reactions are occurring but the four main reaction stages. These are initiation, propagation, hydrogen chain transfer and termination (Blazso, 2006) (Murata, 2004). The product type that is obtainable during plastic pyrolysis can be grouped into two; which are molecules (alkane, alkene etc.) and the free radical. In the optimization of product yield, different factors such structure of plastics and process parameters play a major role. In plastic pyrolysis, these key process parameters such as temperature, type of reactors, pressure, residence time, influences the products obtained.

### Development of Kinetic Models

There are different models that exist that can be used in the prediction of kinetic parameters based on weight loss experiment. Models differ in complexity and shows the variation of the mathematical function used in describing them. Various models have been suggested by different researchers in the literature and all are modelling is done based on kinetics. Kinetic models are mathematical functions developed from assumptions regarding reactants shape and the reaction driving force and these can be identified based on reaction mechanism. Degradation kinetics and pyrolysis mechanism is quite complex and is still being discussed and studied. To give a proper description of the decomposing mixture is difficult and much more in the presence of a catalyst. Thermogravimetry analysis

(TGA) is a thermal analysis method that can help in the determination of weight loss and kinetics parameters as a function of temperature or time. It is the thermal degradation of sample in an inert condition at the same time, measuring the weight loss with increasing temperature while keeping the heating rate constant (Richardson, 2012). The instrument that is used for the continuous weighing of a sample as a function of temperature is the thermobalance and it consist of recording balance, furnace, furnace temperature programmer or controller and recorder. As the temperature is increased, the products are formed during the scission of chemical bonds and non-isothermal experiments ends in complete conversion of the sample into degraded product with residue from carbon. The plot of weight vs temperature is called the thermogravimetric curve. The factors that influence the TGA analysis are sample size and geometry, Atmospheric effect and heating rate.

### Kinetics Analysis of Thermogravimetric Data

Kinetics for degradation reaction process can either be isothermal or non-isothermal. For this study, the TGA experiments were carried out in non-isothermal condition. Rate of decomposition is dependent on temperature  $T$  and  $\alpha$ .  $\alpha$  describes the overall transformation that the reactant progresses. This transformation process involves numerous reactions, each with its specific extent of conversion. Thus,  $\alpha$  can be described as the conversion which is calculated from total weight loss and is defined as follows (VYAZOVKIN, et al., 2011):

$$\alpha = \frac{m_0 - m_T}{m_0 - m_f} \quad (1.1)$$

Where;

- $m_0$  is the initial sample mass (kg);
- $m_T$  is the remaining sample mass at temperature  $T$  (kg);
- $m_f$  is the final mass (kg).

Thus, in thermogravimetric analysis, thermal decomposition of feedstock under above stated conditions can be defined as:

$$\frac{d\alpha}{dt} = K(T) f(\alpha) \quad (1.2)$$

Where;

- $K(T)$  is the temperature dependent rate constant

- $f(\alpha)$  is the conversion function dependent on the reaction mechanism.
- $d\alpha/dt$  is the transformation rate

Rate constant can be defined by Arrhenius equation as follows:

$$K(T) = Ae^{-\left(\frac{E}{RT}\right)} \quad (1.3)$$

Where;

- A is the pre-exponential factor or frequency factor ( $\text{min}^{-1}$ );
- E is the activation energy of the decomposition reaction (kJ/mol);
- R is the universal gas constant (8,314 J/mol);
- T is the absolute temperature (Kelvin)

Thus, combining equation (1.2) and (1.3) produces the basic expression for the study of kinematics of heterogeneous solid-state thermal decomposition

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)} f(\alpha) \quad (1.4)$$

Similarly, the decomposition rate equation can be written as

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{dt}{dT} \quad (1.5)$$

Where;

- $\beta = \frac{dT}{dt}$  is the heating rate (K/min);

The decomposition rate equation can be expressed as function of temperature

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\left(\frac{E}{RT}\right)} f(\alpha) \quad (1.6)$$

Thus, equation (1.6) can be used in describing the thermal decomposition of the feedstock for non-isothermal TGA experiments with constant heating rate

### Determination of Kinetic Parameters

**Direct Arrhenius Plot Method:** This method, follows the equation below (Alonso, 2016):

$$\ln \left[ \frac{1}{(1-\alpha)^n} \frac{\partial \alpha}{\partial T} \right] = \ln \left( \frac{A}{\beta} \right) - \left( \frac{E}{RT} \right) \quad (1.7)$$

For further simplification, and evaluation of the X and Y parameters can be defined as:

$$Y = \ln \left( \frac{A}{\beta} \right) - \left( \frac{E}{R} \right) X \quad (1.8)$$

**Coats and Redfern:** This is a method for estimating kinetic parameters using an integrated form of the rate equation depending on the assumption of n-order kinetics ( $n \neq 1$ ) or the assumption of first order reaction mechanism ( $n=1$ ). (Mostafa ME, 2015)

**For  $n \neq 1$ :**

$$\ln \left[ \frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left( \frac{AR}{\beta T} \right) - \frac{E}{RT} \quad (1.9)$$

**For  $n=1$ :**

$$\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta T} \right) - \frac{E}{RT} \quad (1.10)$$

**Horowitz and Metzger:** This approach assumes that during pyrolysis reaction, no intermediates are formed, all products are gases, which escaped immediately. This model is based on a combination of the reaction rate dependence on both concentration and temperature. The general equation for this model is given below.

$$\ln \frac{W}{W_0} = -e^{-\left(\frac{E_a \theta}{RT_s^2}\right)} \quad (1.11)$$

Where;

- $W = W_t$  = sample weight.
- $W_0$  is the initial weight.
- $T_s$  is reference temperature

**Distributed Activated Energy Method:** This model, assumes that pyrolysis of complex material is a first order decomposition with different chemical group and each group is characterized by its own unique activation energy for the decomposition process. In this model, the activation energy is said to follow a distribution function along the degradation process. The most commonly used distribution function is Gaussian distribution. General equation for DAEM is as follows (Scott, 2006):

$$1 - \frac{V}{V^*} = X = \int_0^\infty \exp(-A \int_0^t e^{-\frac{E_0 t}{RT}} * \delta t) f(E) \partial E \quad (1.12)$$

Where

- $f(E)$  is the distribution function of activation energy

- X is the ratio of volatile that is released at specific temperature to the total volatile released
- V is the total volatiles released
- V\* is the volatile released at a specific temperature

Since Gaussian activation energy distribution is assumed, f(E) can be defined as:

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \quad (1.13)$$

DAEM is quite a complex method in determination of kinetic parameters and the complexity lies in the double integration the general equation hence it is difficult to find an exact mathematical solution. Because of this complexity, obtaining the kinetic parameters can either be by distribution free or distribution fitting.

## 2. MATERIALS AND METHODS

### Plastics

For this study, the plastics obtained comprises of disposable cups, Coca-Cola bottle, drinking water bottles, different kinds of plastics bags, straws, cover of water bottles and disposable spoons and fork obtained from municipal solid waste (MSW) of Portuguese households. Reference polymer materials (PET, LDPE, PS, NYLON & ABS) was obtained from a plastic company. The plastics was washed, dried and sorted accordingly based on polymer type.

### Plastic Characterization

#### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of plastics was carried out using TG-DTA/DSC sateram lab in Nitrogen atmosphere. The experimental trials was initiated at a temperature of 25°C with heating rate of 30°C/min and ended at about 1100°C.

#### Determination of Kinetic Parameters

All the data obtained for the different values of n will be fitted. The n with the best fit line based on highest correlation coefficient will be considered as the correct value of reaction order.

Once the order of reaction n has been calculated, the activation energy and pre-exponential/frequency factor can be calculated.

## Kinetics Modelling

Once the results from thermogravimetric analysis was obtained, it was used in computing an algorithm that reproduced similar result with the experimental results from thermogravimetric analysis. This algorithm was coded using Math Lab, all code was generated using the equations below. The activation energy for this study was calculated using the equation below (Scott, 2006)

$$\frac{1}{B_1} \left[ T_0 e^{\left(\frac{-E_i}{RT_0}\right)} - \frac{E_i}{R} \int_{\frac{E}{RT_0}}^{\infty} \frac{e^{-u}}{u} du - T_1 e^{\left(\frac{-E_i}{RT_1}\right)} + \frac{E_i}{R} \int_{\frac{E}{RT_1}}^{\infty} \frac{e^{-u}}{u} du \right] = \frac{1}{B_2} \left[ T_0 e^{\left(\frac{-E_i}{RT_0}\right)} - \frac{E_i}{R} \int_{\frac{E}{RT_0}}^{\infty} \frac{e^{-u}}{u} du - T_2 e^{\left(\frac{-E_i}{RT_2}\right)} + \frac{E_i}{R} \int_{\frac{E}{RT_2}}^{\infty} \frac{e^{-u}}{u} du \right] \quad (3.1)$$

After determination of the activation energy  $E_i$ , to obtain the pre-exponential factor,  $A_i$ , the value below can be used based on the assumption that the dominating reaction is at some conversion. The conversion refers to individual component and not overall conversion of mass of plastics to volatile material.

$$X = 1 - \frac{1}{e} \Rightarrow \Psi_i = \frac{1}{e} \approx 0.368 \quad (3.2)$$

Thus, for this study the pre-exponential factor,  $A_i$ , was calculated using the equation below (Scott, 2006)

$$\ln(\Psi_i) = -1 = \frac{A_i}{B_1} \left[ T_0 e^{\left(\frac{-E_i}{RT_0}\right)} - \frac{E_i}{R} \int_{\frac{E}{RT_0}}^{\infty} \frac{e^{-u}}{u} du - T_2 e^{\left(\frac{-E_i}{RT_2}\right)} + \frac{E_i}{R} \int_{\frac{E}{RT_2}}^{\infty} \frac{e^{-u}}{u} du \right] \quad (3.3)$$

## 3. RESULTS AND DISCUSSION

### Plastic Characterization

#### Thermogravimetry Analysis

The weight loss curve (TG-DTG) (Fig.1) shows the loss of mass with temperature at 30°C/min heating rate for all plastics types used in this study and the maximum degradation was achieved within 450–520°C. The plot shows that all plastic type exhibit similar temperature behavior, same shape of the decomposition curves which is the single step decomposition. Single step decomposition indicates the presence of carbon-carbon bond that promotes the random scission mechanism with an increase in temperature (Miandad, 2019).

## Determination of Kinetic Parameters

Table 1 shows comparison of activation energy between the different models and known result based on literatures. Variation in the results obtained, could stem from the way in which the integral method have been derived. Graphical methods equations were developed by assuming kinetic parameters from Arrhenius equation, is determined by a form of  $g(X)$ , which is usually assumed.  $X$ , which is a function of both temperature and conversion, and it varies simultaneously with time. Hence, the model cannot distinguish separately temperature dependence of rate constant and the conversion. As a result of this, any model assumed can be easily fit with the experimental data not taking into consideration the variation between assumed model and the true unknown model. Force fitting of the experimental data to the hypothetical reaction can lead to obtaining ambiguous values of Arrhenius parameters.

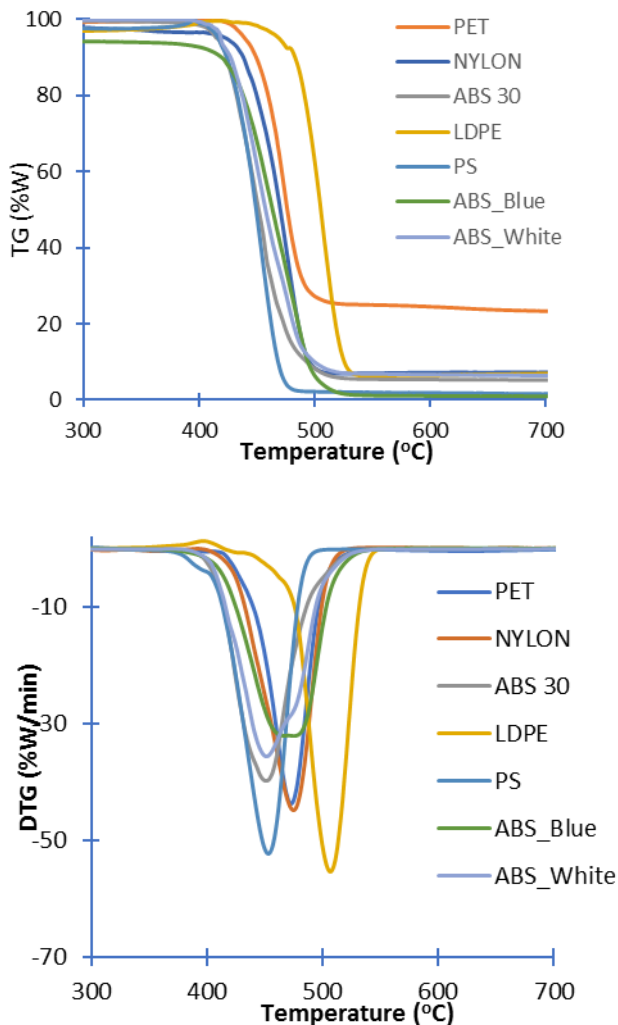


Figure 1: Thermogravimetric Analysis (TG-DTG) of plastic wastes (30°C/min)

Also, for the graphical approach model, different authors have established that this model predicts kinetic parameters quite well for a single first order reaction. However, the model tends to be inadequate in describing complex materials. Coat & Redfern model may be inadequate in providing the proper description for non-isothermal pyrolysis because the kinetic parameters depend on specific polymer used in the experiment and order of reaction this limits the model.

Another reason for variation of kinetic parameters is the possibility of multi-reaction mechanisms with different activation energies as each step, this is influenced by temperature and extent of conversion. Thus, activation energy obtained is a function of  $T$  and  $X$ . From the results obtained, the calculated value of activation energy, represents the average value for the overall degradation process. The value was obtained based on the assumption that these kinetic parameters do not change with reaction mechanism. However, kinetics changes as temperature change so an average kinetic parameter, is not a true representation hence the reason for the distributed activation energy model.

For Horowitz and Metzger model it assumes that all products from the polymer degradation were gaseous and escaped immediately. This assumption made this model simple, but it is not realistic. Taking that into consideration, there is a possibility that the decomposition rate for this model are higher; thus, the activation energy obtained by this model might be lower as compared to the results from literature.

Some variations of results obtained with literature values could be due to differences in the experimental procedure for different samples (such as particle size of sample) and weighing the effects with the data analysis techniques used in the calculation of the kinetic parameters

## Distributed Activation Energy Model

### Comparison of Experimental Result with Simulated Result

The peak in DTG curve indicates a reaction taking place. So, simulation of the exact position of this peak was done using Gaussian distribution. The size of each peak for the different plastics was determined by adjusting the simulated peak temperature, peak height or intensity and peak width to fit the experimental results obtained by thermogravimetric analysis. Solver was used in the optimization of the Gaussian distribution parameters for the different DTG profiles as shown in (Fig 2). From the plot, the simulated result obtained using Gaussian equation was able to

replicate experimental results. However, for some plastic, some discrepancies can be observed such as overprediction or underprediction of the result. Plastics differ in structure and during manufacturing process some additives may have in added. Thus, during the

degradation process, there is the possibility of reaction occurring making this process unique and different from normal distributive curve which Gaussian equation mirrors.

Table 1: Comparison of Activation energies

Plastic Polymer	Activation Energy (kJ/mol)			
	Direct Arrhenius	Coat & Redfern	Horowitz & Metzger	Published data
ABS_White	219	226	138	163.3-248.95
ABS_Blue	240	189	151	163.3-248.95
ABS (30)	188	224	135	163.3-248.95
PS	222	282	142	158.15-200
LDPE	260	275	184	192- 247
NYLON	175	186	167	80-190
PET	304	347	168	180-241

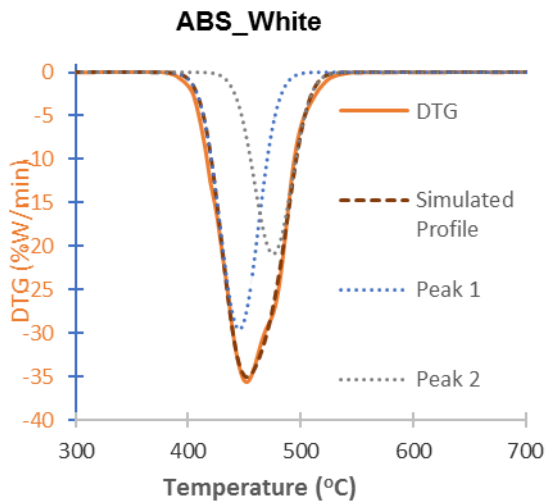


Figure 2: Gaussian distribution curves fitted on DTG experimental results

### Determination of Kinetic Parameters

Kinetic parameters, for the different plastics was determined using the distributed activation energy model (DAEM). This method of approach assumes that the reaction proceed through infinite number of parallel reactions each having its own activation energy. Variation in this activation energy can be shown as a continuous distribution function (Fig 3.). Evaluation of kinetic parameters can either be by distribution free method or distribution fitting method. Gaussian

distribution was used in describing the activation energy for this study. DAEM algorithm was run for about 100 reactions. The activation energy E obtained for ABS\_White, ABS (30) and ABS\_Blue ranged from 128.26 – 186.63, 125.56 – 186.13 and 132.46 – 248.43 KJ/mol, with average activation energy of 166.566, 168.208 and 217.565 kJ/mol respectively. However, the conversion range differ with ABS\_White and ABS (30) within the range of 0.05 – 0.5 and 0.5 – 0.9(Fig 4) while ABS\_ Blue within the range of 0.05 – 0.6 and 0.6 – 0.9. Activation energy obtained for PS, LDPE, PET and NYLON ranged from 127.28 – 209.54, 148.19 – 260.18, 152.36 – 270.38 and 130.93 – 220.61 kJ/mol. Average activation energy calculated was 186.570, 225.7, 235.638 and 191.111 kJ/mol. All average results obtained using DAEM, is in accordance with published data. Comparing the kinetic parameters obtained with Coat & Redfern, Direct Arrhenius method, it can be observed that the activation energy obtained using these methods results can be found with this continuous distribution for a particular conversion. However, DAEM was able to capture the kinetic parameters as a function of temperature.

### Predicting Kinetic Behavior of Plastics

Based on Gaussian distribution curve fitted on experimental data from the best fitted plot with negligible error, kinetic behavior of ABS\_White, NYLON and PET was predicted for different heating rate. (Fig 5) shows the plot of the derivative

thermogravimetric analysis (DTG) for the aforementioned plastics at 15°C/min and 45°C/min heating rate in comparison to the experimental heating rate(30°C/min). From the plot, it can be observed that the shape and peak of simulated results matches the experimental results for all plastics. Heating rate affect the thermal profile of material. An increase in the heating rate, increases the initial, final temperature and

the peak temperature. From the plot, it can be observed that increasing the heating rate, causes the DTG curve to become bigger and peak temperature becomes higher.

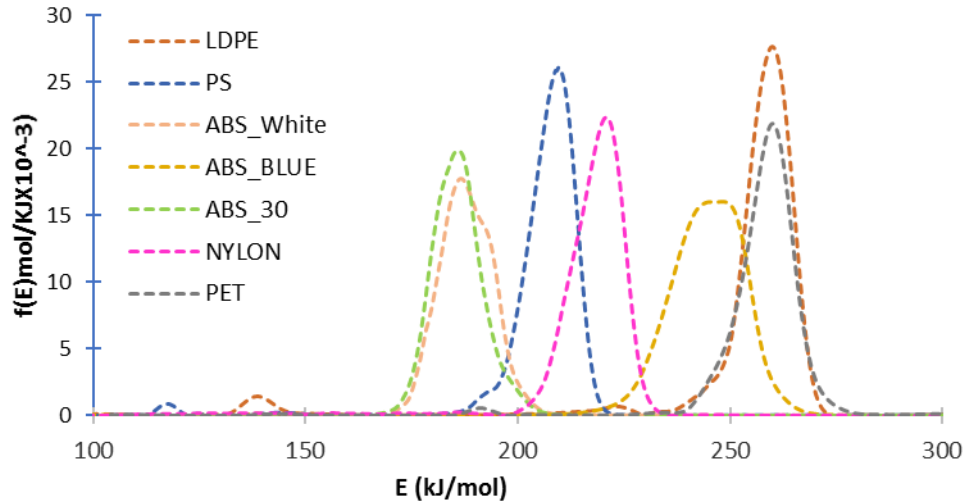


Figure 3: Activation Energy Distribution

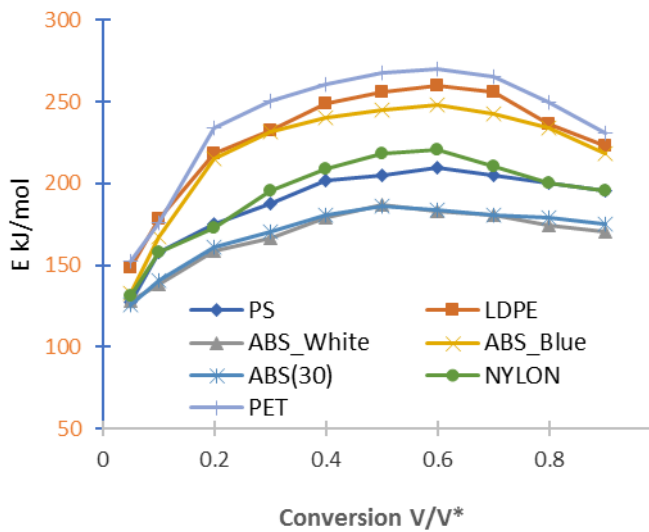


Figure 4: Relationship between activation energy and conversion(V/V\*)

#### 4. CONCLUSIONS

Plastics seems to be part of our daily lives and this contribute to approximately 10% of discarded waste

and only about 25% is being recycled. Annual waste generated is expected to increase by 70% to about 3.4 billion tonnes in 2050 due to rapid increase in population and urbanization. Currently it is very difficult to find an alternative to plastic and the question is what is done after its useful life. Energy plays an important role in the life cycle of plastics. With the increasing demand for energy, the world is faced with finding the right fuel that would not deplete finite stock but also reduce environmental concerns. From the sustainability point of view, energy used in production should be recovered by at the end of the useful life of a product. Pyrolysis of waste plastic seems to be the most suitable method in terms of economics in solving the steadily increasing growing amount of plastic waste and meeting the growing energy demand. Pyrolysis is a complex process and for this process to be done efficiently, understanding the kinetics of the reaction is vital. In this study, the different plastic waste was characterized by their absorption band using the FTIR analysis. Thermogravimetric analysis (TGA) was used in the



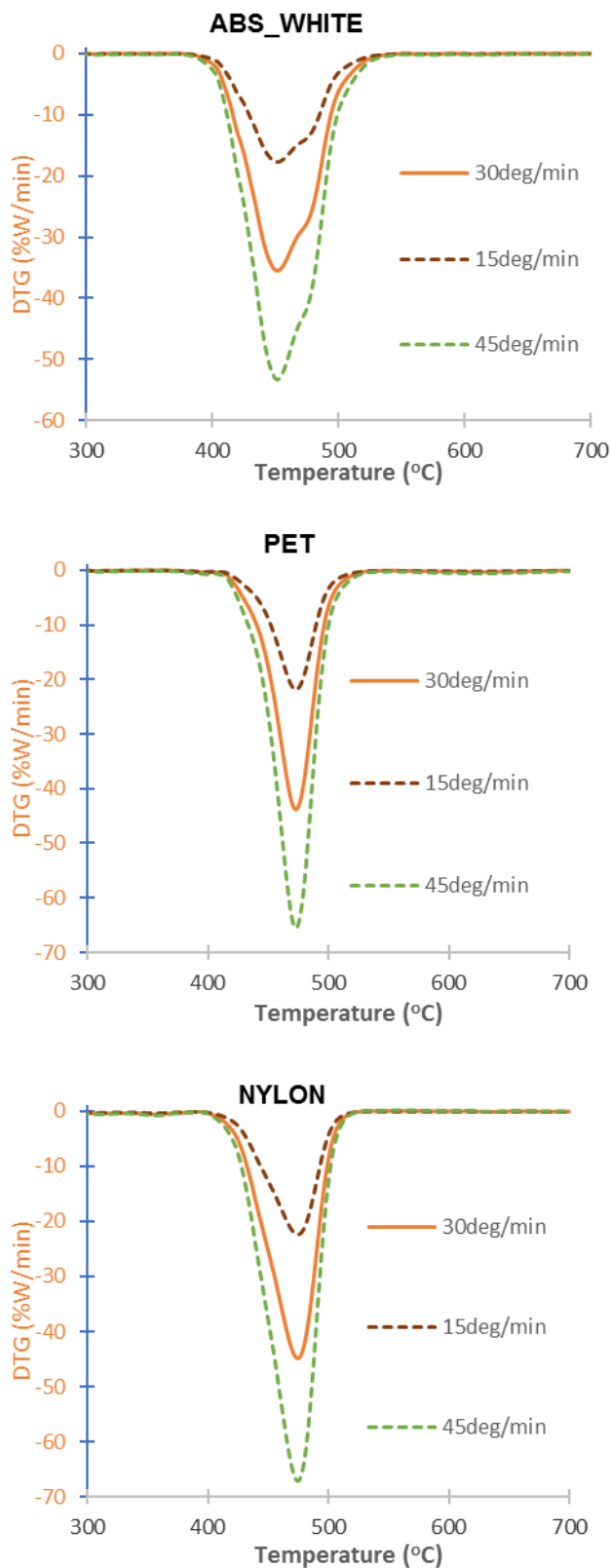


Figure 5: DTG prediction at different heating rate

evaluation of thermal decomposition behavior of the plastics. The maximum degradation was achieved

within 450–520°C with single step decomposition which indicates the presence of carbon-carbon bond that promotes the random scission mechanism with an increase in temperature. Different models exist that can be used in the prediction of kinetic parameters based on thermogravimetric analysis and they differ based on the mathematical function used in describing them. Kinetic parameters for this study was obtained using Direct Arrhenius Method, Coat & Redfern and Horowitz and Metzger. The result obtained using these models was within the range of result obtained from literatures.

However, these mathematical models use unrealistic assumptions that may not be accurate in predicting the true pyrolysis behavior of the polymer, hence it cannot give a proper understanding of how pyrolysis occur and how the process can be optimized thus the reason for the distributed activation energy model (DAEM)

Distributed Activation energy model assumes that pyrolysis of complex fuel is a first order decomposition with different chemical group and each group is having its own unique activation energy for the decomposition process. Activation energy is said to follow a continuous distribution function and for this study, it was the Gaussian distribution. The DAEM algorithm was developed using MATLAB and data obtained from TGA experiments which was used in calculation of kinetic parameters. The results obtained from the simulation was able to effectively model the degradation behavior of the different plastics in this study, thus, predicted the thermal behavior of plastics at different heating rates. However, errors could occur in kinetic parameters obtained when several reactions are occurring simultaneously at the chosen conversion. In addition to this the model is effective in prediction when there no secondary reaction taking place during the degradation process. Aside these shortcomings, DAEM for this study, has proven to be best method in the evaluation of kinetic parameters and all the results obtained using this method was in accordance with published data.

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